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(54) **Lithographic printing members for use with laser irradiation imaging apparatus**

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Plaques lithographiques pour emploi dans un appareil pour produire des images par irradiation au laser

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(56) References cited:
EP-A- 0 580 393 **EP-A- 0 644 047**

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to lithographic printing plates.

[0002] Traditional techniques of introducing a printed image onto a recording material include letterpress printing, gravure printing and offset lithography. All of these printing methods require a plate, usually loaded onto a plate cylinder of a rotary press for efficiency, to transfer ink in the pattern of the image.

[0003] In the case of offset lithography, the image is present on a plate or mat as a pattern of ink-accepting (oleophilic) and ink-repellent (oleophobic) surface areas. In a dry printing system, the plate is simply inked and the image transferred onto a recording material; the plate first makes contact with a compliant intermediate surface called a blanket cylinder which, in turn, applies the image to the paper or other recording medium. In typical sheet-fed press systems, the recording medium is pinned to an impression cylinder, which brings it into contact with the blanket cylinder.

[0004] The plates for an offset press are usually produced photographically. To prepare a wet plate using a typical negative-working subtractive process, the original document is photographed to produce a photographic negative. This negative is placed on an aluminum plate having a water-receptive oxide surface coated with a photopolymer. Upon exposure to light or other radiation through the negative, the areas of the coating that received radiation (corresponding to the dark or printed areas of the original) cure to a durable oleophilic state. The plate is then subjected to a developing process that removes the uncured areas of the coating (i.e., those which did not receive radiation, corresponding to the non-image or background areas of the original), exposing the hydrophilic surface of the aluminum plate.

[0005] A similar photographic process is used to create dry plates, which typically include an ink-abhesive (e.g., silicone) surface layer coated onto a photosensitive layer, which is itself coated onto a substrate of suitable stability (e.g., an aluminum sheet). Upon exposure to actinic radiation, the photosensitive layer cures to a state that destroys its bonding to the surface layer. After exposure, a treatment is applied to deactivate the photoresponse of the photosensitive layer in unexposed areas and to further improve anchorage of the surface layer to these areas. Immersion of the exposed plate in developer results in dissolution and removal of the surface layer at those portions of the plate surface that have received radiation, thereby exposing the ink-receptive, cured photosensitive layer.

[0006] Photographic platemaking processes tend to be time-consuming and require facilities and equipment adequate to support the necessary chemistry. To circumvent these shortcomings, practitioners have developed a number of electronic alternatives to plate imaging, some of which can be utilized on-press. With these systems, digitally controlled devices alter the ink-receptivity of blank plates in a pattern representative of the image to be printed. Such imaging devices include sources of electromagnetic-radiation pulses, produced by one or more laser or non-laser sources, that create chemical changes on plate blanks (thereby eliminating the need for a photographic negative); ink-jet equipment that directly deposits ink-repellent or ink-accepting spots on plate blanks; and spark-discharge equipment, in which an electrode in contact with or spaced close to a plate blank produces electrical sparks to physically alter the topology of the plate blank, thereby producing "dots" which collectively form a desired image (see, e.g., U.S. Patent No. 4,911,075). Because of the ready availability of laser equipment and their amenability to digital control, significant effort has been devoted to the development of laser-based imaging systems. Early examples utilized lasers to etch away material from a plate blank to form an intaglio or letterpress pattern. See, e.g., U.S. Patent Nos. 3,506,779; 4,347,785. This approach was later extended to production of lithographic plates, e.g., by removal of a hydrophilic surface to reveal an oleophilic underlayer. See, e.g., U.S. Patent No. 4,054,094. These systems generally require high-power lasers, which are expensive and slow.

[0007] European Patent Specification No. 0 580 393 A2 relates to wet and dry, two and three layer lithographic printing plates. In the two layer plates, the first layer is ablatable by absorption of imaging infra-red radiation, while in the three layer plates, the second layer is partially transmissive and ablatable. In both types of plate, reflecting means is provided for reflecting back into the ablation layer a substantial portion of the imaging infra-red radiation incident thereon. The reflecting means may be formed from a metal, possibly aluminum layer.

[0008] European Patent Specification No. 0 644 047 A2 (prior art according to Art.54(3)(4) EPC) describes lithographic printing members having secondary ablation layers for use with laser-discharge imaging apparatus. The members have a topmost first layer and a second layer underneath the topmost layer for ablative absorption of laser radiation. A third layer underlying the second layer is ablated only partially in response to ablation of the second layer. The second layer may be a composite including titanium oxide and aluminum layers.

[0009] According to the present invention, there is provided a lithographic printing member as defined in claim 1 below.

[0010] It is an aim of the invention to provide lithographic printing plates using relatively inexpensive laser equipment that operates at low to moderate power levels. The imaging techniques described herein can be used in conjunction with a variety of plate-blank constructions, enabling production of "dry" plates to which ink is applied directly. As used herein, the term "plate" refers to any type of printing member or surface capable of recording an image defined by

regions exhibiting differential affinities for ink; suitable configurations include the traditional planar or curved lithographic plates that are mounted on the plate cylinder of a printing press, but can also include seamless cylinders (e.g., the roll surface of a plate cylinder), an endless belt, or other arrangement.

[0011] In embodiments of the present invention materials that enhance the ablative efficiency of the laser beam may be used. Substances that do not heat rapidly or absorb significant amounts of radiation will not ablate unless they are irradiated for relatively long intervals and/or receive high-power pulses; such physical limitations are commonly associated with lithographic-plate materials, and account for the prevalence of high-power lasers in the prior art. In one embodiment, which represents the primary subject of the present application. The first, topmost layer is chosen for its affinity for (or repulsion of) ink or an ink-abhesive fluid. Underlying the first layer is a thin metal layer that absorbs IR radiation. A strong, stable substrate underlies the metal layer, and is characterized by an affinity for (or repulsion of) ink or an ink-abhesive fluid opposite to that of the first layer. Exposure of the plate to a laser pulse ablates the absorbing thin metal second layer, weakening the topmost layer as well. As a result of ablation of the thin metal second layer, the weakened surface layer is no longer anchored to an underlying layer, and is easily removed. The disrupted topmost layer (and any debris remaining from destruction of the absorptive second layer) is removed in a post-imaging cleaning step. This creates an image spot having a different affinity for the ink or ink-abhesive fluid than the unexposed first layer.

[0012] Post-imaging cleaning can be accomplished using a contact cleaning device such as a rotating brush (or other suitable means as described in U.S. Patent No. 5,148,746. Although post-imaging cleaning represents an additional processing step, the persistence of the topmost layer during imaging can actually prove beneficial. Ablation of the absorbing layer creates debris that can interfere with transmission of the laser beam (e.g., by depositing on a focusing lens or as an aerosol (or mist) of fine particles that partially blocks transmission). The disrupted but unremoved topmost layer prevents escape of this debris.

[0013] The printing members of the present invention are preferably manufactured for convenient bulk use on automatic plate-material dispensing equipment, such as that described in US PATENT No 5,355,795 (EP-A-0 640 678). Because in such arrangements rolled plate material is stored on a small-diamter core from which it is drawn tightly around the plate cylinder, it is important to utilize materials that are flexible and have low dynamic friction coefficients to accommodate free movement, but which also exhibit the durability required of a lithographic printing member.

[0014] The imaging apparatus of the present invention includes at least one laser device that emits in the IR, and preferably near-IR region; as used herein, "near-IR" means imaging radiation whose $lambda_{max}$ lies between 700 and 1500 nm. In embodiments of the present invention solid-state lasers (commonly termed semiconductor lasers and typically based on gallium aluminum arsenide compounds) may be advantageously used as sources; these are distinctly economical and convenient, and may be used in conjunction with a variety of imaging devices. The use of near-IR radiation facilitates use of a wide range of organic and inorganic absorption compounds and, in particular, semiconductive and conductive types.

[0015] Laser output can be provided directly to the plate surface via lenses or other beam-guiding components, or transmitted to the surface of a blank printing plate from a remotely sited laser using a fiber-optic cable.

[0016] The foregoing discussion will be understood more readily from the following detailed description of the invention, when taken in conjunction with the accompanying drawings, in which:

[0017] FIGS. A and B are enlarged sectional views showing lithographic plates imageable in accordance with the present invention.

[0018] The size of an image feature (i.e., a dot, spot or area) and image resolution can be varied in a number of ways. The laser pulse must be of sufficient power and duration to produce useful ablation for imaging; however, there exists an upper limit in power levels and exposure times above which further useful, increased ablation is not achieved. Unlike the lower threshold, this upper limit depends strongly on the type of plate to be imaged.

[0019] Variation within the range defined by the minimum and upper parameter values can be used to control and select the size of image features. In addition, so long as power levels and exposure times exceed the minimum, feature size can be changed simply by altering the focusing apparatus (as discussed below). The final resolution or print density obtainable with a given-sized feature can be enhanced by overlapping image features (e.g., by advancing the writing array an axial distance smaller than the diameter of an image feature). Image-feature overlap expands the number of gray scales achievable with a particular feature.

[0020] The final plates should be capable of delivering at least 1,000, and preferably at least 50,000 printing impressions. This requires fabrication from durable material, and imposes certain minimum power requirements on the laser sources. For a laser to be capable of imaging the plates described below, its power output should be at least 1.3 megawatt/cm^2 and preferably at least 3.9 megawatt/cm^2. Significant ablation ordinarily does not occur below these power levels, even if the laser beam is applied for an extended time.

[0021] Because feature sizes are ordinarily quite small -- on the order of 12.7 to 50.8 µm (0.5 to 2.0 mils) -- the necessary power intensities are readily achieved even with lasers having moderate output levels (on the order of about 1 watt); a focusing apparatus, as discussed below, concentrates the entire laser output onto the small feature, resulting in high effective energy densities.

Reference EXAMPLES 1-7

[0022] These examples describe preparation of positive-working dry plates that include silicone coating layers and polyester substrates, which are coated with nitrocellulose materials to form the absorbing layers. The nitrocellulose coating layers include thermoset-cure capability and are produced as follows:

Component	Parts
Nitrocellulose	14
Cymel 303	2
2-Butanone (methyl ethyl ketone)	236

The nitrocellulose utilized was the 30% isopropanol wet 5-6 Sec RS Nitrocellulose supplied by Aqualon Co., Wilmington, DE. Cymel 303 is hexamethoxymethylmelamine, supplied by American Cyanamid Corp.

[0023] An IR-absorbing compound is added to this base composition and dispersed therein. Use of the following seven compounds in the proportions that follow resulted in production of useful absorbing layers:

Example	1	2	3	4	5	6	7
Component	Parts						
Base Composition	252	252	252	252	252	252	252
NaCure 2530	4	4	4	4	4	4	4
Vulcan XC-72	4	-	-	-	-	-	-
Titanium Carbide	-	4	-	-	-	-	-
Silicon	-	-	6	-	-	-	-
Heliogen Green L 8730	-	-	-	8	-	-	-
Nigrosine Base NG-1	-	-	-	-	8	-	-
Tungsten Oxide	-	-	-	-	-	20	-
Vanadium Oxide	-	-	-	-	-	-	10

NaCure 2530, supplied by King Industries, Norwalk, CT, is an amine-blocked p-toluenesulfonic acid solution in an isopropanol/methanol blend. Vulcan XC-72 is a conductive carbon black pigment supplied by the Special Blacks Division of Cabot Corp., Waltham, MA. The titanium carbide used in Example 2 was the Cerex submicron TiC powder supplied by Baikowski International Corp., Charlotte, NC. Heliogen Green L 8730 is a green pigment supplied by BASF Corp., Chemicals Division, Holland, MI. Nigrosine Base NG-1 is supplied as a powder by N H Laboratories, Inc., Harrisburg, PA. The tungsten oxide ($WO_{2.9}$) and vanadium oxide (V_6O_{13}) used above are supplied as powders by Cerac Inc., Milwaukee, WI.

[0024] Following addition of the IR absorber and dispersion thereof in the base composition, the blocked PTSA catalyst was added, and the resulting mixtures applied to the polyester substrate using a wire-wound rod. After drying to remove the volatile solvent(s) and curing (1 min at 148°C in a lab convection oven performed both functions), the coatings were deposited at 1 g/m^2.

[0025] The nitrocellulose thermoset mechanism performs two functions, namely, anchorage of the coating to the polyester substrate and enhanced solvent resistance (of particular concern in a pressroom environment).

[0026] The following silicone coating was applied to each of the anchored IR-absorbing layers produced in accordance with the seven examples described above.

Component	Parts
PS-445	22.56
PC-072	.70
VM&P Naphtha	76.70
Syl-Off 7367	.04

(These components are described in greater detail, and their sources indicated, in the patent US-A-5,118,032 and also in U.S. Patent No. 5,212,048 and US Patent 5,310,869; these applications describe numerous other silicone formulations useful as the material of an oleophobic layer 408.)

[0027] We applied the mixture using a wire-wound rod, then dried and cured it to produce a uniform coating deposited

at 2 g/m^2. The plates are then ready to be imaged.

[0028] We have found that a metal layer disposed as illustrated by reference numeral 418 in Fig. A can, if made thin enough, support imaging by absorbing, rather than reflecting, IR radiation. This approach is valuable both where layer 416 absorbs IR radiation (as contemplated in FIG. A) or is transparent to such radiation. In the former case, the very thin metal layer provides additional absorptive capability (instead of reflecting radiation back into layer 416). Furthermore, this type of construction exhibits substantial flexibility, and is therefore well-suited to plate-winding arrangements. Appropriate metal layers are appreciably thinner than the 20-70 nm (200-700 Å) thickness useful in a fully reflective layer.

[0029] One can also employ, as an alternative to a metal reflecting layer, a layer containing a pigment that reflects IR radiation. Once again, such a layer can underlie layer 408 or 416, or may serve as substrate 400. A material suitable for use as an IR-reflective substrate is the white 329 film supplied by ICI Films, Wilmington, DE, which utilizes IR-reflective barium sulfate as the white pigment. In a variation of the construction shown in Fig. A, the reflecting layer is itself the substrate.

[0030] Because such a thin metal layer may be discontinuous, it can be useful to add an adhesion-promoting layer to better anchor the surface layer to the other (non-metal) plate layers. Inclusion of such a layer is illustrated in FIG. B. This construction contains a substrate 400, the adhesion-promoting layer 420 thereon, a thin metal layer 418, and a surface layer 408. Suitable adhesion-promoting layers, sometimes termed print or coatability treatments, are furnished with various polyester films that may be used as substrates. For example, the J films marketed by E.I. duPont de Nemours Co., Wilmington, DE, and Melinex 453 sold by ICI Films, Wilmington, DE serve adequately as layers 400 and 420. Generally, layer 420 will be very thin (on the order of 1 micron or less in thickness) and, in the context of a polyester substrate, will be based on acrylic or polyvinylidene chloride systems.

[0031] In embodiments of the invention, at least one very thin (preferably 25 nm (250 Å) or less) layer of titanium is deposited onto a polyester substrate 400 and coated with an addition-cure silicone (an oleophobic material). Exposure of this construction to a laser pulse ablates the thin metal layer and weakens the topmost layer and destroys its anchorage, rendering it easily removed. The detached topmost layer (and any debris remaining from destruction of the absorptive second layer) is removed in a post-imaging cleaning step.

[0032] Titanium is adopted for the thin-metal layer 418 because it offers a variety of advantages over other IR-absorptive metals. First, titanium layers exhibit substantial resistance to handling damage, particularly when compared with metals such as aluminum, zinc and chromium; this feature is important both to production, where damage to layer 418 can occur prior to coating thereover of 416, and in the printing process itself where weak intermediate layers can reduce plate life. In the case of dry lithography, titanium further enhances plate life through resistance to interaction with ink-borne solvents that, over time, migrate through layer 416; other materials, such as organic layers, may exhibit permeability to such solvents and allow plate degradation. Moreover, silicone coatings applied to titanium layers tend to cure at faster rates and at lower temperatures (thereby avoiding thermal damage to substrate 400), require lower catalyst levels (thereby improving pot life) and, in the case of addition-cure silicones, exhibit "post-cure" cross-linking (in marked contrast, for example, to nickel, which can actually inhibit the initial cure). The latter property further enhances plate life, since more fully cured silicones exhibit superior durability, and also provides further resistance against ink-borne solvent migration. Post-cure cross-linking is also useful where the desire for high-speed coating (or the need to run at reduced temperatures to avoid thermal damage to substrate 400) make full cure on the coating apparatus impracticable. Titanium also provides advantageous environmental and safety characteristics: its ablation does not produce measurable emission of gaseous byproducts, and environmental exposure presents minimal health concerns. Finally, titanium, like many other metals, exhibits some tendency to interact with oxygen during the deposition process (vacuum evaporation, electron-beam evaporation or sputtering); however, the lower oxides of titanium most likely to be formed in this manner (particularly TiO) are strong absorbers of near-IR imaging radiation. In contrast, the likely oxides of aluminum, zinc and bismuth are poor absorbers of such radiation.

[0033] Preferred polyester films for use in this embodiment have surfaces to which the deposited metal adheres well, and exhibit substantial flexibility to facilitate spooling and winding over the surface of a plate cylinder. One useful class of preferred polyester material is the unmodified film exemplified by the MELINEX 442 product marketed by ICI Films, Wilmington, DE, and the 3930 film product marketed by Hoechst-Celanese, Greer, SC. Also advantageous, depending on the metal employed, are polyester materials that have been modified to enhance surface adhesion characteristics as described above. Suitable polyesters of this type include the ICI MELINEX 453 product. These materials accept titanium without the loss of properties. Other metals, by contrast, require custom pretreatments of the polyester film in order to create compatibility therebetween. For example, vinylidenedichloride-based polymers are frequently used to anchor aluminum onto polyesters.

[0034] For traditional applications involving plates that are individually mounted to the plate cylinder of a press, the adhesion-promoting surface can also (or alternatively) be present on the side of the polyester film in contact with the cylinder. Plate cylinders are frequently fabricated from material with respect to which the adhesion-promoting surface exhibits a high static coefficient of friction, reducing the possibility of plate slippage during actual printing. The ICI 561

product and the dupont MYLAR J102 film have adhesion-promoting coatings applied to both surfaces, and are therefore well-suited to this environment.

[0035] For applications involving automatic plate-material dispensing apparatus, however, the ease of winding the material around the cylinder represents an equally important consideration, and favors the use of materials having a low dynamic coefficients of friction with respect to the cylinder. Adhesion-promoting surfaces should not be used on the exterior polyester surface if the result is excessive resistance to movement. On the other hand, antistatic treatments can impart a beneficial reduction of resistance to movement with respect to many surfaces (compared with unmodified polyester). This is particularly true for plate constructions featuring semiconductive layers, which can accumulate static charges that retard free travel along the plate cylinder. Examples of antistatic polyester films include the duPont MYLAR JXM301 and JMX502 products; the latter film includes an adhesion-promoting treatment on its reverse side.

[0036] Ideally, and to the extent practicable, the cylinder and the polyester surface in contact with it are matched to provide low dynamic but high static coefficients of friction. For this reason, it is important to consider both the dynamic and static behavior of any surface treatment in conjunction with a particular type of plate cylinder, and to evaluate this behavior against an unmodified surface.

[0037] The metal layer 418 is preferably deposited to an optical density ranging from 0.2 to 1.0, with a density of 0.6 being especially preferred. However, thicker layers characterized by optical densities as high as 2.5 can also be used to advantage. This range of optical densities generally corresponds to a thickness of 25 nm (250 Å) or less. While titanium is preferred as layer 418, alloys of titanium can also be used to advantage. The titanium or titanium alloy can also be combined with lower oxides of titanium.

[0038] Metals such as titanium may be conveniently applied by well-known deposition techniques such as sputtering, electron-beam evaporation and vacuum evaporation. Depending on the condition of the polyester surface, sputtering can prove particularly advantageous in the ready availability of co-processing techniques (e.g., glow discharge and back sputtering) that can be used to modify polyester prior to deposition.

[0039] Depending on requirements relating to imaging speed and laser power, it may prove advantageous to provide the metal layer with an antireflective overlay to increase interaction with the imaging pulses. The refractive index of the antireflective material, in combination with that of the metal, creates interfacial conditions that favor laser penetration over reflection. Suitable antireflective materials are well-known in the art, and include a variety of dielectrics (e.g., metal oxides and metal halides). Materials amenable to application by sputtering can ease manufacture considerably, since both the metal and the antireflection coating can be applied in the same chamber by multiple-target techniques.

[0040] The coating layer 416 is a silicone composition, for dry-plate constructions. Our preferred silicone formulation is that described earlier in connection with Examples 1-7, applied to produce a uniform coating deposited at 2 g/m^2. The anchorage of coating layer 416 to metal layer 418 can be improved by the addition of an adhesion promoter, such as a silane composition (for silicone coatings).

[0041] Although the foregoing construction is well-suited to plate material intended for automatic-dispensing apparatus, it can also be utilized in composite laminated designs, using, for example, relatively thin (e.g., 0.5 to 3mn) polyester films adhered to a metal or heavy plastic (e.g., a 1.78×10^{-2} cm (7-mil) polyester) support. In a representative production sequence, a 5.1×10^{-3} cm (2-mil) polyester film is coated with titanium and then silicone, following which the coated film is laminated onto an aluminum base having a thickness appropriate to the overall plate thickness desired.

[0042] Lamination confers a number of advantages, chief among which are rigidity of the final construction and the ability to add reflection capability. Lamination facilitates the use of readily available heavy support layers that may contain surface imperfections; by contrast, were such a support used directly as substrate 400, it would be necessary to employ expensive materials specially processed to remove any irregularities. Second, the support layer can serve to reflect unabsorbed imaging radiation that has passed through the absorptive layer and layers thereunder; in the case, for example, of near-IR imaging radiation, aluminum (and particularly polished aluminum) laminated supports provide highly advantageous reflectivity. In this case, substrate 400, the laminating adhesive and any other layers between the absorptive layer and the laminated support (e.g., a primer coat) should be largely transparent to imaging radiation. In addition, substrate 400 should be relatively thin so that beam energy density is not lost through divergence before it strikes the reflective support. For proper operation in conjunction with the laser equipment described hereinabove, polyester substrates, for example, are preferably no thicker than 2 mm.

[0043] Use of a reflective laminated support is particularly useful in the case of plates having titanium absorptive layers, since these tend to pass at least some fraction of incident imaging radiation at the optical densities required for satisfactory performance. Moreover, titanium has been found to respond well to lamination, retaining its adhesion to under- and overlying layers notwithstanding the application of pressure and heat.

[0044] Suitable techniques of lamination are well-characterized in the art, and are disclosed, for example, in the US patent 5,188,032. In our production of printing members, we prefer to utilize materials both for substrate 400 and for the support in roll (web) form. Accordingly, roll-nip laminating procedures are preferred. In this production sequence, one or both surfaces to be joined are coated with a laminating adhesive, and the surfaces are then brought together under pressure and, if appropriate, heat in the nip between cylindrical laminating rollers.

[0045] Laminating adhesives are materials that can be applied to a surface in an unreactive state, and which, after the surface is brought into contact with a second surface, react either spontaneously or under external influence. In the present context, a laminating adhesive should possess properties appropriate to the environment of the present invention. As noted above, the adhesive should not absorb imaging radiation, both to permit reflection and to avoid undergoing thermal damage as a consequence of absorption; this is readily achieved for near-IR imaging radiation as discussed below. Another useful property is a refractive index not significantly different from that of the substrate 400 (which also, as earlier noted, should be largely transparent to imaging radiation).

[0046] In one embodiment, the laminating adhesive is thermally activated, consisting of solid material that is reduced to a flowable (melted) state by application of heat; resolidification results in bonding of the layers (i.e., substrate 400 and the support) between which the adhesive is sandwiched. Heat is supplied by at least one of the two rollers that form the laminating nip, and may be augmented by preheating in advance of the nip. The nip also supplies pressure that creates a uniform area contact between the layers to be joined, expelling air pockets and encouraging adhesive flow.

[0047] In a first approach, adhesive may be applied as a solid (i.e., as a powder that is thermally fused into a continuous coating, or as a mixture of fluid components that are cured to a solid state following application) to one or both of the two surfaces to be joined; for example, a solid adhesive can be applied as a melt via extrusion coating at elevated temperatures, preferably at a thickness of 12.7 to 25.4 μm (0.5-1.0 mil). Following application, the adhesive is chilled and resolidified. Adhesives suitable for this approach include polyamides, copolymers of ethylene and vinyl acetate, and copolymers of ethylene and acrylic acid; specific formulas, including chemical modifications and additives that render the adhesive ideally suited to a particular application, are well-characterized in the art.

[0048] In a second approach, the adhesive is applied as a waterborne composition. In this case, it may be useful to treat the application surface to promote wetting and adhesion of waterborne materials. For example, in the case of a polyester substrate 400 that is to receive such a laminating adhesive, wettability can be improved by prior treatment with one or more polymers based on polyvinylidene dichloride.

[0049] In a third, preferred approach, the adhesive layer is cast from a solvent onto one or both of the two surfaces to be joined. This technique facilitates substantial control over the thickness of the applied layer over a wide range, and results in good overall surface contact and wetting onto the surface to which it is applied. Adhesives of this type can include cross-linking components to form stronger bonds and thereby improve cohesive strength, as well as to promote chemical bonding of the adhesive to at least one of the surfaces to be joined (ordinarily to a polymeric layer, such as a polyester substrate 400 and/or a heavy polyester support via reaction with terminal hydroxyl groups). They can also be formulated to include a reactive silane (i.e., a silane adhesion promoter) in order to chemically bond the adhesive to an aluminum support.

[0050] One useful family of laminating adhesives that may be cast is based on polyester resins, applied as solvent solutions, and which include a cross-linking component. A useful example of such a formulation is as follows:

Component	Parts
Vitel 3550	36
MEK (2-butanone)	64
Prepare solution, then add, just prior to coating:	
Mondur CB-75	4.5

Vitel 3550 is a polyester resin supplied by Shell Chemical Co., Akron, OH. Mondur CB-75 is an isocyanate cross-linker supplied by Mobay Chemical Corp., Pittsburgh, PA.

[0051] This formulation is applied to the unprocessed side of a titanium-metallized, silicone-coated polyester film as described above, and the MEK solvent is evaporated using heat and air flow. The wet application rate is preferably chosen to result in a final dried weight of 10+/- g/m^2. However, it should be emphasized that a wide range of application weights will produce satisfactory results, and the optimal weight for a given application will depend primarily on the materials chosen for the support and substrate 400.

[0052] The adhesive-coated film is laminated to an aluminum substrate of desired thickness, preferably using roll-nip lamination under heat and pressure.

[0053] An alternative to thermally activated laminating adhesives is the class of pressure-sensitive adhesives (PSAs). These are typically cast from a solvent onto the unprocessed side of substrate 400, dried to remove solvent, and finally laminated under pressure to a support. For example, the roll-nip laminating procedure described above can be utilized with no heat applied to either of the rollers. As in the case of thermally activated adhesives, post-application cross-linking capability can be included to improve bonding between surfaces and of the adhesive to the surfaces. The adhesive can also be applied, either in addition or as an alternative to application on substrate 400, to the support.

The PSA can be provided with additives to promote adhesion to the support, to substrate 400, or to both.

[0054] Like thermally activated adhesives, PSAs can be applied as solids, as waterborne compositions, or cast from solvents. Once again, pre-treatment of an application surface to enhance wettability may prove advantageous.

[0055] We note that it is also possible to add a near-IR absorbing layer in order to eliminate any need for IR-absorption capability in surface layer 408, but where a very thin metal layer alone provides insufficient absorptive capability.

[0056] Any of a variety of production sequences can be used advantageously to prepare the plates shown in FIGS. A and B. In one representative sequence, substrate 400 (which may be, for example, polyester or a conductive polycarbonate) is metallized to form reflective layer 418, and then coated with silicone or a fluoropolymer (either of which may contain a dispersion of IR-absorptive pigment) to form surface layer 408; these steps are carried out as described, for example, in the US patent 5,165,345 in connection with FIGS. 4F and 4G.

[0057] Alternatively, one can add a barrier sheet to surface layer 408 and build up the remaining plate layers from that sheet. A barrier sheet can serve a number of useful functions in the context of the present invention. First, as described previously, those portions of surface layer 408 that have been weakened by exposure to laser radiation must be removed before the imaged plate can be used to print. Using a reverse-imaging arrangement, exposure of surface layer 408 to radiation can result in its molten deposition, or decaling, onto the inner surface of the barrier sheet; subsequent stripping of the barrier sheet then effects removal of superfluous portions of surface layer 408. A barrier sheet is also useful if the plates are to include metal bases (as described in the US patent 5,188,032), and are therefore created in bulk directly on a metal coil and stored in roll form; in that case surface layer 408 can be damaged by contact with the metal coil.

[0058] A representative construction that includes such a barrier layer, shown at reference numeral 427, is depicted in FIG. B; it should be understood, however, that barrier sheet 427 can be utilized in conjunction with any of the plate embodiments discussed herein. Barrier layer 427 is preferably smooth, only weakly adherant to surface layer 408, strong enough to be feasibly stripped by hand at the preferred thicknesses, and sufficiently heat-resistant to tolerate the thermal processes associated with application of surface layer 408. Primarily for economic reasons, preferred thicknesses range from 6.35×10^{-4} to 5.1×10^{-3} cm (0.00025 to 0.002 inch). Our preferred material is polyester; however, polyolefins (such as polyethylene or polypropylene) can also be used, although the typically lower heat resistance and strength of such materials may require use of thicker sheets.

[0059] Barrier sheet 427 can be applied after surface layer 408 has been cured (in which case thermal tolerance is not important), or prior to curing; for example, barrier sheet 427 can be placed over the as-yet-uncured layer 408, and actinic radiation passed therethrough to effect curing.

[0060] One way of producing the illustrated construction is to coat barrier sheet 427 with a silicone material (which, as noted above, can contain IR-absorptive pigments) to create layer 408. This layer is then metallized, and the resulting metal layer coated or otherwise adhered to substrate 400. This approach is particularly useful to achieve smoothness of surface layers that contain high concentrations of dispersants which would ordinarily impart unwanted texture.

[0061] It will therefore be seen that we have developed a highly versatile imaging system and a variety of plates for use therewith.

Claims

1. A lithographic printing member directly imageable by laser irradiation, the member comprising:

   a first layer which is formed of an addition-cure silicone;
   a thin metal layer directly underlying the first layer and formed of titanium or an alloy thereof; and
   a substrate underlying the metal layer; wherein
   the metal layer is subject to ablative absorption of imaging infrared radiation and the first layer is not; and
   the first layer and the substrate exhibit different affinities for at least one printing liquid selected from the group consisting of ink and an abhesive fluid for ink.

2. A lithographic printing member according to claim 1, wherein the metal layer is of a thickness of less than 25nm (250Å).

3. A lithographic printing member according to claim 1 or claim 2, wherein the metal layer has an optical density ranging from 0.2 to 1.0.

4. A lithographic printing member according to claim 1 or claim 2, wherein the metal layer has an optical density of 2.5 or less.

5. A lithographic printing member according to any one of the preceeding claims, wherein the substrate comprises first and second surfaces, at least one of which includes adhesive means for adhesion.

6. A lithographic printing member according to any one of the preceeding claims, wherein the substrate comprises first and second surfaces, at least one of said first and second surfaces including static-buildup reducing means.

7. A lithographic printing member according to claim 4, wherein the substrate comprises first and second surfaces, one of which first and second surfaces includes adhesive means and the other of which first and second surfaces includes static-buildup reducing means.

8. A lithographic printing member according to any one of the preceeding claims, including a metal support to which the substrate is laminated.

9. A lithographic printing member according to any one of the preceeding claims, wherein the substrate comprises a material that reflects imaging radiation.

10. A lithographic printing member according to claim 9, wherein the material is an infra-red reflective barium sulphate.

11. A lithographic printing member according to claim 10, wherein the substrate comprises a polyester polymer within which the barium sulphate is dispersed.

Patentansprüche

1. Flachdruckelement, das durch Laserstrahlung direkt belichtbar ist, wobei das Element aufweist:

   eine erste Schicht, die aus einem durch Zusatzmittel härtbaren Silicon gebildet wird;

   eine direkt unter der ersten Schicht liegende dünne Metallschicht aus Titan oder einer Titanlegierung;

   ein unter der Metallschicht liegendes Substrat; wobei

   die Metallschicht einer abtragenden Absorption von Infrarot-Abbildungsstrahlung ausgesetzt wird und die erste Schicht der Absorption nicht ausgesetzt wird; und

   die erste Schicht und das Substrat unterschiedliche Affinitäten zu mindestens einer Druckflüssigkeit aufweisen, die aus der Gruppe ausgewählt ist, die aus Druckfarbe und einem farbabweisenden Fluid besteht.

2. Flachdruckelement nach Anspruch 1, wobei die Metallschicht eine Dicke von weniger als 25 nm (250 Å) aufweist.

3. Flachdruckelement nach Anspruch 1 oder Anspruch 2, wobei die Metallschicht eine optische Dichte im Bereich von 0,2 bis 1,0 aufweist.

4. Flachdruckelement nach Anspruch 1 oder Anspruch 2, wobei die Metallschicht eine optische Dichte von höchstens 2,5 aufweist.

5. Flachdruckelement nach einem der vorstehenden Ansprüche, wobei das Substrat eine erste und eine zweite Oberfläche aufweist, von denen mindestens eine ein Klebemittel zum Ankleben aufweist.

6. Flachdruckelement nach einem der vorstehenden Ansprüche, wobei das Substrat eine erste und eine zweite Oberfläche aufweist, wobei mindestens eine von den ersten und zweiten Oberflächen ein antistatisches Mittel aufweist.

7. Flachdruckelement nach Anspruch 4, wobei das Substrat eine erste und eine zweite Oberfläche aufweist, wobei mindestens eine von den ersten und zweiten Oberflächen ein Klebemittel aufweist, während die andere von den ersten und zweiten Oberflächen ein antistatisches Mittel aufweist.

8. Flachdruckelement nach einem der vorstehenden Ansprüche mit einem Metallträger, auf den das Substrat auflaminiert ist.

9. Flachdruckelement nach einem der vorstehenden Ansprüche, wobei das Substrat ein Material aufweist, das Abbildungsstrahlung reflektiert.

10. Flachdruckelement nach Anspruch 9, wobei das Material ein infrarotreflektierendes Bariumsulfat ist.

11. Flachdruckelement nach Anspruch 10, wobei das Substrat ein Polyesterpolymer aufweist, in dem das Bariumsulfat dispergiert ist.

Revendications

1. Elément d'impression lithographique pouvant directement donner une image par un rayonnement laser, l'élément comprenant:

   une première couche qui est constituée d'une silicone de durcissement par addition;

   une couche mince métallique directement sous-jacente à la première couche et constituée de titane ou d'un alliage de celui-ci; et

   un substrat sous-jacent à la couche métallique; dans lequel

   la couche métallique est soumise à une absorption ablative d'un rayonnement infrarouge produisant une image et la première couche ne l'est pas; et

   la première couche et le substrat montrent différentes affinités pour au moins un liquide d'impression choisi dans le groupe constitué d'une encre et d'un fluide non collant pour une encre.

2. Elément d'impression lithographique suivant la revendication 1, dans lequel la couche métallique possède une épaisseur inférieure à 25 nm (250 Å).

3. Elément d'impression lithographique suivant la revendication 1 ou la revendication 2, dans lequel la couche métallique présente une densité optique variant de 0,2 à 1,0.

4. Elément d'impression lithographique suivant la revendication 1 ou la revendication 2, dans lequel la couche métallique présente une densité optique inférieure ou égale à 2,5.

5. Elément d'impression lithographique suivant l'une quelconque des revendications précédentes, dans lequel le substrat comprend une première et une seconde surfaces, dont au moins une inclut un moyen adhésif en vue d'une adhérence.

6. Elément d'impression lithographique suivant l'une quelconque des revendications précédentes, dans lequel le substrat comprend une première et une seconde surfaces, au moins une desdites première et seconde surfaces incluant un moyen réducteur de l'accumulation statique.

7. Elément d'impression lithographique suivant la revendication 4, dans lequel le substrat comprend une première et une seconde surfaces, dont une des première et seconde surfaces inclut un moyen adhésif et dont l'autre des première et seconde surfaces inclut un moyen réducteur de l'accumulation statique.

8. Elément d'impression lithographique suivant l'une quelconque des revendications précédentes, incluant un support métallique auquel le substrat est laminé.

9. Elément d'impression lithographique suivant l'une quelconque des revendications précédentes, dans lequel le substrat comprend un matériau qui réfléchit un rayonnement produisant une image.

10. Elément d'impression lithographique suivant la revendication 9, dans lequel le matériau est du sulfate de baryum réfléchissant l'infrarouge.

11. Elément d'impression lithographique suivant la revendication 10, dans lequel le substrat comprend un polymère

de polyester à l'intérieur duquel le sulfate de baryum est dispersé.

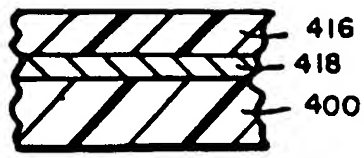

FIG. A

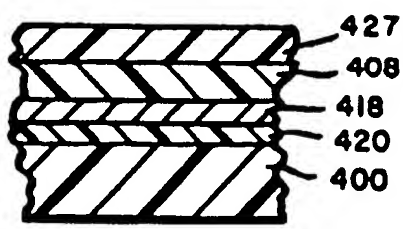

FIG. B